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(54) Title: ADDITIVES ENABLING BLENDING OF POLAR AND NON-POLAR FUEL COMPONENTS

**(57) Abstract**

This invention relates to novel alternative liquid fuels for internal combustion engines. More specifically, this invention relates to the use of inexpensive vegetable oil-derived chemicals to permit the blending of liquid fuels such as diesel or gasoline with components such as wet ethanol to produce an alternative fuel for internal combustion engines. A liquid fuel for use in diesel engines comprising: (a) about 37 to 96 % wt. diesel fuel; (b) about 0.1 to about 37 % wt. hydrous alcohol; and (c) an effective amount of a non-ionic surfactant used either alone or in combination with one or more fatty acids and their ammonium salts, the combination of ingredients adding up to 100 %.

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ADDITIVES ENABLING BLENDING OF POLAR  
AND NON-POLAR FUEL COMPONENTS

FIELD OF THE INVENTION

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This invention relates to novel alternative liquid fuels for internal combustion engines. More specifically, this invention relates to the use of inexpensive vegetable oil-derived chemicals to permit the blending of liquid fuels such as diesel or gasoline with components such as wet ethanol to produce an alternative fuel for internal combustion engines.

BACKGROUND OF THE INVENTION

15

Hydrocarbons are a non-renewable resource and are expected to run out in the 21st Century. Rising costs due to increasing scarcity of non-renewable hydrocarbon liquid fuels for internal combustion engines, and the like, have even today, provided a strong incentive to develop acceptable, inexpensive, modified or alternative fuels, particularly utilizing renewable resources.

Hydrocarbon fuels have another disadvantage. The use of many hydrocarbon fuels, such as diesel, results in high particulate and NOX emissions. The presence of these pollutants presents significant health risks wherever diesel fuel is used in quantity.

A major problem with developing modified or alternative fuels, however, is that most of the liquid fuel candidates available from renewable resources have a chemical character that is incompatible with existing hydrocarbon fuels. Another problem is that, for practical and economical reasons, it is very difficult to convert the huge internal combustion engine industry entirely from one type of liquid fuel to another. It would therefore be advantageous if the alternative fuel resembled diesel or gasoline as closely as possible. Thus, as one alternative,

it would be attractive if it were possible to mix proportions of several fuel components into "hybrid" fuels that could be used in standard internal combustion engines without modification.

5

Hybrid fuels provide a challenge in that to be able to formulate a "hybrid" fuel, a way must be devised to mix what are prima facie incompatible liquids. The theory behind being able to develop such hybrid formulations must be based on chemical structure and associated affinities. Some work in this area has been done in the past.

10

It is known, for instance, that diesel oil can be blended with fatty acid triglycerides such as degummed soybean oil in any proportion to produce a blend that is suitable for use in diesel engines for short periods of time. However, it was found that prolonged use of such a blend in a diesel engine leads to carbon build-up and contamination of crankcase oil. Such a blend also does not appear to improve the quality of engine emissions (Goldkist, 1981).

20

It is also known that C<sub>1</sub>-C<sub>4</sub> alcohols (methanol, ethanol, propanol and butanol) can be blended up to 20% volume with gasoline but cannot be blended with diesel fuel alone. It is now evident that such alcohols, especially methanol and ethanol, can be produced from renewable resources at costs that are below the energy equivalent cost of gasoline or diesel oil in many places. This has resulted in the use of these components in blends with or as substitutes for gasoline. Blends of alcohol and gasoline described as "gasohol" are used in the U.S.A., Brazil, and many other countries. However, the use of alcohols in diesel blends is more complex and would require the incorporation of one or more compatible components to the blend to confer stability.

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The prior art reveals efforts by various inventors to incorporate polar compounds such as water and alcohol with nonpolar diesel fuel and gasoline by use of surfactants. McCoy et al., U.S. Patent No. 3,876,391, granted April 8, 1975, describes the use of pairs of water-soluble and gasoline-soluble surfactants to enable the blending of polar additives with gasoline. Examples of such polar additives include formamide, acetamide, ethylene glycol, urea, ethylene diamine, propylene diamine, meta-phenylene diamine and formaldehyde. However, they did not include C<sub>1</sub>-C<sub>4</sub> alcohols.

Wenzel et al., U.S. Patent No. 4,002,435, granted January 11, 1977, discloses the concept to blending diesel fuel by employing a complex four component surfactant mixture consisting of (1) a branched chain primary alkanol having 13-16 carbon atoms, (2) a mixture of ammonium and sodium oleate, (3) an organic fatty acid, and (4) an ethylene oxide condensation product to enable the incorporation of up to 10% water. The objective is to alter the combustion characteristics of straight diesel fuel to improve engine wear and quality of emissions. Wenzel et al. do not disclose the incorporation of C<sub>1</sub>-C<sub>4</sub> alcohols. The presence of sodium salts in the fuel mixture is problematic since such salts generate a corrosive ash.

Broeck et al., U.S. Patent No. 4,002,437, granted January 11, 1977, avoid the use of sodium but nonetheless disclose a complex mixture of surfactant chemicals comprising: (1) dimeric and trimeric acids, (2) an amine salt of an oxo-alkyl acid ester of ortho-phosphoric acid, and (3) an aliphatic demulsifier of alkoxyated fatty acids to improve combustion characteristics.

Piotrowski, U.S. Patent No. 4,046,519, describes the incorporation of 2-19% vol. methanol into gasoline using a 9:1 mixture of diglycerides of oleic acid and

bis(hydroxy-ethyl)stearyl amine oxide. All examples disclosed employ surfactant mixtures rich in nitrogen which probably contribute to undesirable NOX emissions.

5           None of the foregoing discussed patents disclose the incorporation of C<sub>1</sub>-C<sub>4</sub> alcohols as a class into hydrocarbon fuels nor do they address the cost and complexity of the multi-component surfactant mixtures employed.

10           Later, Wenzel et al., in U.S. Patent No. 4,083,698, granted April 11, 1978, describes an emulsion incorporating 10% vol. methanol and diesel fuel using their above-described complex formulation of surfactants. The  
15           patent states that ethanol or isopropyl alcohol can be substituted for methanol but there are no specific examples supporting this assumption. The emulsions incorporating methanol with diesel fuel were unstable at low temperatures unless a mixture of cyclohexanol/cyclohexanone was added.

20           Boehmke, U.S. Patent No. 4,297,107, granted October 27, 1981, describes the use of a non-ionic surfactant comprising the addition product of ethylene oxide or propylene oxide and a carboxylic acid amide with  
25           9-21 carbon atoms for the purpose of incorporating water into hydrocarbon fuels. The patent mentions the incorporation of alcohols only as an afterthought. Nitrogenous ingredients are again employed that could contribute to NOX emissions.

30           U.S. Patent No. 4,445,908 entitled "Extracting Alcohols from Aqueous Solutions", discloses a procedure for recovering mixed C<sub>1</sub>-C<sub>4</sub> alcohols directly from fermentation broths for use in fuels. There is no disclosure of the fuel formulations, per se, using mixed C<sub>1</sub>-C<sub>4</sub> alcohols.

35           Lepain, in U.S. Patent No. 4,477,258, granted October 15, 1984, discloses the formation of stable water-

in-oil emulsions using a minor amount of an aqueous methanol or ethanol solution stabilized by a blend of sorbitan monooleate and an ethoxylated, non-ionic surfactant. The surfactants employed are costly.

5

Schwab, U.S. Patent No. 4,451,265, granted May 29, 1984, discloses the use of a surfactant system comprising N,N-dimethylethanolamine and a long chain fatty acid to enable the blending of aqueous alcohols with diesel. The N,N-dimethylethanolamine is nitrogenous and could contribute to increasing NOX emissions. It is also costly.

10

Hazbun et al., in U.S. Patent No. 4,744,796, granted May 17, 1978, and U.S. Patent No. 4,770,670, granted September 13, 1988, disclose the use of another mixture of either tertiary butyl alcohol or phenyl alcohol with an ionic or non-ionic surfactant for blending water and/or methanol with hydrocarbon fuels for the purpose of altering flammability characteristics to address safety concerns in certain special applications. The use of such emulsions as transportation fuels is not addressed nor is there reference to the use of aqueous ethanol. Such emulsions would also be costly.

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#### SUMMARY OF THE INVENTION

The invention is directed to the formation of a stable emulsion between polar and non-polar components using vegetable oil compounds having an affinity for both. This affinity enables the production of stable fuel emulsions of polar and non-polar components that are less expensive than conventional hydrocarbon fuels and exhibit reduced particulate and nitrogen oxide (NOX) emissions.

30

35

The invention is directed to a liquid fuel for use in diesel engines comprising: (a) about 37 to 96% wt. diesel fuel; (b) about 0.1 to about 37% wt. hydrous alco-

hol; and (c) an effective amount of a non-ionic surfactant used either alone or in combination with one or more fatty acids and their ammonium salts, the combination of ingredients adding up to 100%. The hydrous alcohol can  
5 contain about 5% water.

The hydrous alcohol can be selected from the group consisting of methanol, ethanol, propanol and butanol. The hydrous alcohol can be hydrous ethanol. The  
10 hydrous alcohol can contain about 5% wt. water.

The non-ionic surfactant can be selected from the group consisting of alkoxyphenol, sorbitan monooleate, oleodiethanolamide and glyceryl monooleate. The non-ionic  
15 surfactant can be oleodiethanolamide or glyceryl monooleate.

The diesel fuel can comprise about 37 to 96% wt., the hydrous alcohol can be hydrous ethanol and can comprise  
20 about 2 to about 37% wt., and the non-ionic surfactant can be oleodiethanolamide comprising about 27 to 39% wt., the total amount of the components adding up to 100%.

The diesel fuel can comprise about 37 to 96% wt.,  
25 the hydrous alcohol can be hydrous ethanol and can comprise about 2 to about 37% wt., and the non-ionic surfactant can be glyceryl monooleate comprising about 2 to 39% wt., the total amount of the components adding up to 100%.

30 The fatty acid can be oleic acid comprising about 9 to 11% wt. The fuel can include about 1% wt. ammonium hydroxide. The fatty acid can be oleic acid comprising about 13 to 16% wt. and the fuel can contain about 1 to 3% wt. ammonium hydroxide.

35 The invention is also directed to a liquid fuel for use in diesel engines comprising: (a) 41 to 59% wt.



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diesel fuel; (b) 2 to about 31% wt. hydrous ethanol; and (c) 27 to 39% wt. oleodiethanolamide.

5 In another aspect, the invention is directed to a liquid fuel for use in diesel engines comprising: (a) 37 to 59% wt. diesel fuel; (b) 2 to about 38% wt. hydrous ethanol; and (c) 2 to 39% wt. glyceryl monooleate.

10 The invention also pertains to a method of extending diesel fuel for use in diesel engines which comprises adding to pure diesel fuel between about 0.1% to about 37% wt. hydrous alcohol and an effective amount of a non-ionic surfactant to form a hybrid fuel emulsion which is stable and does not separate into phases at temperatures  
15 above -12°C. The hydrous alcohol can be hydrous ethanol containing about 5% wt. water.

The non-ionic surfactant can be selected from the group consisting of butyl phenoxy  $(CH_2CH_2O)_nH$  wherein n can  
20 be between about 9 to about 15, sorbitan monooleate, polyoxyalkynol fatty acid ester, oleodiethanolamide, and glyceryl monooleate.

The method can include an effective amount of a  
25 fatty acid. The fatty acid can be oleic acid. The fatty acid can be in the form of an ammonium salt fatty acid. The fuel can include ammonium hydroxide or glyceryl monooleate.

30 DETAILED DESCRIPTION OF SPECIFIC  
EMBODIMENTS OF THE INVENTION

Hybrid Fuels for Diesel Engines

35 The invention is directed to a family of vegetable oil/wet ethanol/diesel ("hybrid") fuel emulsions

that can be used as direct substitutes for pure diesel fuel.

5 The inventors herein have been able to produce a family of alternative fuels that (1) reduce particulate and NOX emissions, (2) extend fossil hydrocarbon fuel resources with ingredients derived from renewable resources, and (3) are usable without modification to existing internal combustion engines. In one aspect, the invention focuses  
10 on formulations that are simple and economical.

A very important feature of the invention is that the emulsions permit the use of wet ethanol (190 proof) in place of pure ethanol. This is a major advantage because  
15 it eliminates the need for azeotropic distillation of ethanol, which is a costly processing step that limits the economical feasibility of small scale production. Many vegetable oils are in abundant supply, are energy-rich and, in many cases, are available at attractive prices,  
20 especially if they enable the use of cheap wet ethanol (rather than expensive anhydrous ethanol) as a fuel extender.

The use of diesel fuel, particularly in urban  
25 areas, generates high levels of particulates and nitrogen oxide (NOX) emissions. The hybrid fuels of the invention alter the combustion characteristics in a positive way. Harmful emissions are reduced without engine conversion, or complex changes in existing internal combustion engine fuel  
30 distribution channels.

It seems to be a fact of nature and typical of the field of chemistry that chemical groups having certain similarities attract while chemical groups that have  
35 certain differences repel. To lend some order to the whole field, it has been customary over time for chemists to place chemical substances into different classes. One of

the principal traditional and longstanding classifications of chemical species has been into "polar" and "non-polar" groups, even though such a classification may not be strictly quantifiable based on fundamental principles. Nevertheless, the classification is helpful in many cases. As a general rule, polar substances will tend to mix well with one another if they have a similar make-up. Likewise, non-polar substances will tend to mix with one another. Diesel fuel is an example of a "non-polar" substance. However, as a general rule, "polar" and "nonpolar" substances tend not to mix with one another.

Water, ethanol and other alcohols, on the other hand, are "polar". Partially hydrolyzed vegetable oil is somewhat of a hybrid because it has both "polar" and "non-polar" groups, making it somewhat of a surfactant. It is possible that the "polar"/"non-polar" character of a vegetable oil derivative might enable it to draw together "non-polar" diesel fuel and "polar" wet alcohol thereby allowing the two latter substances to mix in the correct proportions for use as alternative fuels. An advantage of this, assuming it can be done, would be that vegetable oil surfactants are inexpensive to manufacture and, if the concept proves out, would allow the manufacture and use of wet ethanol and methanol in diesel fuel blends to provide a family of alternative fuels that are less expensive than pure diesel.

The addition of clearly flammable liquids, such as ethanol, to diesel fuel should alter the combustion characteristics of diesel such that the blends exhibit reduced particulate and NOX emissions. Thus, the ability to form stable emulsions of renewable and hydrocarbon fuel components over a broad range of concentrations would open the possibility for making "hybrid" fuels that have substantial environmental, as well as cost benefits.

The subject invention defines a reliable methodology for the incorporation of wet ethanol, and wet C<sub>1</sub>-C<sub>4</sub> alcohols in general, into diesel fuel utilizing a single, inexpensive surfactant, preferably nitrogen-free. This is accomplished by using a family of vegetable oil derived surfactants that, when used alone, have the ability to emulsify polar aqueous alcohols with non-polar diesel fuel by virtue of the fact that the surfactants have polar hydroxyl group functionalities as well as non-polar alkane chains. Such suitable inexpensive vegetable oil derived surfactants employ simple production technology and are abundant, low cost feedstocks.

In one embodiment, the invention relates to the production of a clear, temperature stable emulsion fuel suitable for use in a diesel engine comprising:

- (a) 37 - 80% wt. diesel fuel;
- (b) 0.1 - 37% wt. hydrous C<sub>1</sub>-C<sub>4</sub> alcohol containing about 5% wt. water; and
- (c) an effective amount of a non-ionic surfactant used either alone or in combination with fatty acids and their ammonium salts, the total summing to 100%.

The formulation procedure involves mixing one or more of the non-ionic surfactants with hydrous alcohol to form a mixture with a uniform consistency. If free fatty acid or its ammonium salt is to be used, it is added to the mixture and mixed to uniform consistency. This is followed by the addition of diesel fuel to the mixture, and further mixing until a homogeneous emulsion is achieved. The components can be blended in a different sequence with the same end result. No special mixing or emulsification procedures are required to obtain a homogeneous emulsion.

35

The invention enables the incorporation of up to 37% vol. hydrous C<sub>1</sub>-C<sub>4</sub> alcohols in diesel fuel. The emul-

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sions exhibit reasonable cold stable to  $-20^{\circ}\text{C}$  (depending on proportions used) and exhibit marked reductions in particulate and NOX emissions when tested in diesel engines. No design modifications to the diesel engines are  
5 required.

The invention in one embodiment focuses on vegetable oils as extenders or partial substitutes for pure diesel fuel.

10

A significant advantage of our invention is that an emulsion according to our invention, with only modest modifications, allows increased wet ethanol content in company with low cost industrial-grade ingredients. We  
15 have discovered that as an initial composition, an inexpensive alkoxyphenol surfactant combined with industrial grade oleic acid and a small amount of ammonia enables the preparation of 2:1 emulsion blends having up to 10% wt. wet ethanol content. The emulsion is stable above  $5^{\circ}\text{C}$  and can  
20 be rendered stable to minus  $12^{\circ}\text{C}$  by adding 5% cyclohexanol and cyclohexanone. At distributor bulk prices, the emulsion is calculated to be 25% more expensive than pure diesel fuel.

25

Having demonstrated the viability of the basic principle, a range of alternative surfactants and oils have been tested in comparison to the original formulation employing an alkoxyphenol surfactant. Alternative surfactants have been selected that more closely mimic the  
30 chemical structure of the other ingredients.

We have found that one surfactant, Mazamide-DEA, in terms of wet alcohol content, performs better than the first tested alkoxyphenol surfactant. We have discovered  
35 that emulsion formulations using Mazamide-DEA surfactant can carry as much as 30% wt. wet ethanol and are stable to minus  $12^{\circ}\text{C}$  without additives or ammonia. Mazamide-DEA is

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made up of oleic acid (a vegetable oil acid) linked to ethanol by an ammonia (amide) group. Another advantage is that with the reduced nitrogen content of the emulsion, the potential for generating NOX emissions from nitrogen is reduced. Due to the higher cost of the surfactant, however, the mixed fuel formulation is calculated to cost 20% more than pure diesel fuel.

We have further discovered that industrial grade glyceryl monooleate (GMOI) is a suitable surfactant for purposes of the invention. It is inexpensive since it is simply partly-hydrolyzed vegetable oil. Moreover, its chemical structure embodies the necessary invention criteria. To our surprise, GMOI proved on testing to provide a dramatic improvement compared to Mazamide-DEA, and an even greater improvement over the original alkoxy-phenol surfactant. The GMOI formulations allowed a content of as much as 38% wt. wet ethanol in the emulsion. The formulations were stable to -12°C, and contained no nitrogen whatsoever. We also discovered that as much as two thirds of the diesel fuel could be displaced with GMOI/wet ethanol.

The GMOI product of commerce is actually a mixture, containing 45-55% monooleate with lesser amounts of di and trioleate. It was further found that more pure glyceryl monooleate performed better than GMOI, requiring less to emulsify a given amount of hydrous ethanol and exhibiting better cold stability. Glyceryl monooleate of greater than 90% purity which was obtained by direct synthesis, proved able to create a stable diesel emulsion with a given amount of hydrous ethanol using only one third the amount. This enabled the formulation of emulsions stable to 0°C containing 9.6% wt. hydrous ethanol using only 12.8% wt. of purified glyceryl monooleate. By increasing the glyceryl monooleate content by only 1.2%, emulsions could be rendered stable to -15°C.

The cost of the formulation would be about 10% above pure diesel. However, there would be a high potential for further cost reductions since GMOI is simple to make, and costs of making it would be lowered at high production rates. The cost of an emulsion containing 10% wt. hydrous ethanol using GMOI (at distributor bulk prices) is approximately 10% greater than pure diesel fuel. If purified glyceryl monooleate could be manufactured at a comparable cost, then the cost of the corresponding emulsion would be equal to that of pure diesel fuel. Although the cost of glyceryl monooleate manufacture by direct synthesis would most likely be greater than current GMOI production methods, research has shown that a more pure glyceryl monooleate product can also be produced by methanol extraction of commercial GMOI. It is plausible to consider the retrofit of an extraction system at existing GMOI plants that could make a more pure product available without a significant increase in production cost.

Well-positioned manufacturers of vegetable oil and ethanol would be able to reduce costs by increasing production and thereby produce hybrid fuel at competitive prices. Prospects of success for the invention should be particularly good for landlocked countries. Such countries should preferably have abundant vegetable oil and fermentable feedstocks and currently import all or most of their diesel fuel requirements. The surfactant, GMOI, in particular, would be suitable because it could be manufactured in large quantities in the most rudimentary type oil processing plant.

The production of wet ethanol, rather than pure ethanol, also involves simplified technology. This is a strong advantage since, for purposes of the invention, anhydrous ethanol is not required. Hybrid fuels according to the invention therefore appear to be a viable option for small-scale, on-farm and developing country situations.

The following examples demonstrate various emulsion formulations that were prepared according to the invention.

5

Example 1Use of Hydrous Ethanol with Polyethoxy Alkyl Phenol  
and Oleic Acid/Ammonium Oleate in Diesel Fuel

10 Alkoxyphenol (Tergitol NP-9 through 15<sup>TM</sup>)  
surfactant of the general structure, butyl phenoxy-  
(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>H, where n = 9 to 15, was blended with oleic acid,  
28% ammonium hydroxide and hydrous (190 proof) ethanol  
15 until a homogeneous mixture was achieved. Diesel fuel was  
then added and mixed to the following final proportions:

	<u>Component</u>	<u>Wt. % of Mixture</u>
	NP-9 - 15 Surfactant	11
	Oleic Acid	10
20	Ammonium Hydroxide	1.1
	Hydrous Ethanol	9 - 15
	Diesel	63 - 69

25 The mixture was clear and stable at room temperature. The phases separate after refrigerating for 24 hours at -12°C. The phases remixed on warming to 0°C. The phase separation upon chilling could be prevented by the addition of an anti-freeze such as 5 wt. % of a 5.7:1 mixture of cyclohexanol/cyclohexanone.

30

The cost of the emulsion at distributor bulk prices was calculated to be 25% greater than the current cost of diesel fuel.



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Example 2Hydrous Ethanol with Sorbitan Monooleate and  
Oleic Acid/Ammonium Oleate in Diesel Fuel

5

Sorbitan monooleate (PPG-S-MAZ80) surfactant was blended with oleic acid, 28% ammonium hydroxide and hydrous (190 proof) ethanol until a homogeneous mixture was achieved. Diesel fuel was then added and mixed to the following final proportions:

<u>Component</u>	<u>Wt. % of Mixture</u>
Sorbitan Monooleate Surfactant	11
Oleic Acid	10
Ammonium Hydroxide	1.1
Hydrous Ethanol	9 - 15
Diesel	63 - 69

The mixture was clear and stable at room temperature. The phases did not separate after refrigeration for 24 hrs. at -12°C.

Example 3

25

Hydrous Ethanol with Polysorbate 60 and  
Oleic Acid/Ammonium Oleate in Diesel Fuel

Polysorbate 60 (Tween 60™, a polyoxyalkanol fatty acid ester) surfactant was blended with oleic acid, 28% ammonium hydroxide and hydrous (190 proof) ethanol until a homogeneous mixture is achieved. Diesel fuel was then added and mixed to the following final proportions:

<u>Component</u>	<u>Wt. % of Mixture</u>
Polysorbate 60 Surfactant	11
Oleic Acid	10
Ammonium Hydroxide	1.1

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Hydrous Ethanol	9
. Diesel	69

5 The mixture was clear and stable at room temperature. The phases did not separate after refrigeration for 24 hrs. at  $-12^{\circ}\text{C}$ .

#### Example 4

#### 10 Hydrous Ethanol with Oleyldiethanolamide and Oleic Acid/Ammonium Oleate in Diesel Fuel

15 Oleyldiethanolamide (Mazamide SS-10<sup>TM</sup>) surfactant was blended with oleic acid, 28% ammonium hydroxide and hydrous (190 proof) ethanol until a homogeneous mixture was achieved. Diesel fuel was then added and mixed to the following final proportions:

	<u>Component</u>	<u>Wt. % of Mixture</u>
20	Oleyldiethanolamide Surfactant	11
	Oleic Acid	10
	Ammonium Hydroxide	1.1
	Hydrous Ethanol	9 - 27
	Diesel	51 - 69

25

The mixture was clear and stable at room temperature. The phases did not separate after refrigeration for 24 hrs. at  $-12^{\circ}\text{C}$  over the range of ethanol concentrations.

30

#### Example 5

#### Hydrous Ethanol with Oleyldiethanolamide and Oleic Acid in Diesel Fuel

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This example was similar to Example 4. Oleyldiethanolamide (Mazamide SS-10<sup>TM</sup>) surfactant was blended with oleic acid, hydrous (190 proof) ethanol until

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a homogeneous mixture was achieved. Diesel fuel was then added and mixed to the following final proportions:

	<u>Component</u>	<u>Wt. % of Mixture</u>
5	Oleyldiethanolamide Surfactant	11
	Oleic Acid	9
	Hydrous Ethanol	15 - 28
	Diesel	52 - 65

10           The mixture was clear and stable at room temperature over the percentages shown. The phases did not separate after refrigeration for 24 hrs. at -12°C until the ethanol concentration exceeded 25%.

15           A major advantage of this formulation over prior formulations is that the use of ammonia has been eliminated. This should beneficially lower adverse NOX emissions.

20           At the maximum ethanol concentration attainable, the emulsion was calculated to cost 20% more than pure diesel fuel at distributor wholesale prices.

#### Example 6

25

#### Hydrous Ethanol with Oleyldiethanolamide in Diesel Fuel

30           Oleyldiethanolamide (Mazamide SS-10™) surfactant was blended with hydrous (190 proof) ethanol until a homogeneous mixture was achieved. Diesel fuel was then added and mixed to the following final proportions:

	<u>Component</u>	<u>Wt. % of Mixture</u>
35	Oleyldiethanolamide Surfactant	27 - 39
	Hydrous Ethanol	2 - 31
	Diesel	41 - 59

- 18 -

The mixture was clear and stable at room temperature. The phases did not separate after refrigeration for 24 hrs. at -12°C.

5 A major advantage of this formulation is that only a single surfactant is employed. Complex surfactant combinations are not necessary.

Example 7

10

Hydrous Ethanol with Glyceryl  
Monooleate in Diesel Fuel

15 Glyceryl monooleate (GMOI) surfactant was blended with diesel fuel until a homogeneous mixture was achieved. Hydrous (190 proof) ethanol was then added and mixed to the following final proportions:

	<u>Component</u>	<u>Wt. % of Mixture</u>
20	Glyceryl Monooleate Surfactant	25 - 39
	Hydrous Ethanol	2 - 38
	Diesel	37 - 59

25 The mixture was clear and stable at room temperature. The phases did not separate after refrigeration for 24 hrs. at -12°C until the ethanol concentration exceeded 25%.

30 The foregoing formulation is particularly advantageous because it employs only a single surfactant and does not include any nitrogen containing substances. This should lead to reduced NOX emissions.

35 An economic analysis (at distributor bulk prices) shows this emulsion to cost only 10% more than the current retail price of diesel fuel. Well-positioned manufacturers

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of bulk vegetable oil and ethanol should therefore be able to produce this "hybrid fuel" at competitive prices.

5 The reason that the amounts of surfactant in Examples 6 and 7 are higher than in Examples 1 to 5 is because they enable stable emulsions to be formed over a broader range of ethanol concentrations. Also, their simplicity and low cost make it feasible for these components to be used in greater proportions as economical  
10 substitutes for diesel fuel. In Examples 1 to 5, the surfactants work over a more narrow range of ethanol concentrations. Also, their expense prohibits their use in large amounts.

15

Example 8

Hydrous Methanol with Glyceryl  
Monooleate in Diesel Fuel

20

Industrial glyceryl monooleate (GMOI) surfactant was blended with hydrous methanol containing 5% wt. water until a homogeneous mixture was achieved. Diesel fuel was then added and mixed to the following final proportions:

25

<u>Component</u>	<u>Wt. % of Mixture</u>
Glyceryl Monooleate Surfactant	30
Hydrous Methanol	10
Diesel	60

30

The mixture was clear and stable at room temperature. The phases did not separate after refrigeration for 24 hrs. at 0°C. At room temperature, up to 1% wt. of water could be added before phase separation was noted.

35

Methanol is currently the least expensive of the alcohols. Although it is currently manufactured by the

- 20 -

reforming of natural gas, it can also be made from renewable resources by biomass gasification.

#### Example 9

5

#### C<sub>3</sub> and C<sub>4</sub> Alcohols with Glyceryl Monooleate in Diesel Fuel

Industrial glyceryl monooleate (GMOI) was first  
10 mixed with the anhydrous alcohol (a), (b) or (c) where (a)  
is n-propyl alcohol, (b) is iso-propyl alcohol and (c) is  
n-butyl alcohol, until a homogeneous mixture was achieved.  
Diesel fuel was then added to the mixture and mixed to the  
following final proportions:

15

<u>Component</u>	<u>Wt. % of Mixture</u>
Glyceryl Monooleate Surfactant	30
Anhydrous Alcohol (a), (b) or (c)	10
Diesel	60

20

0.5% wt. water was then added dropwise with mixing. In all  
cases, a stable emulsion was obtained at room temperature  
although it appeared to take longer for water to disperse  
in the emulsion containing n-butyl alcohol. The emulsions  
25 were stable down to a temperature of 10°C but solids gelled  
out upon chilling at 7°C for 6 days.

#### Example 10

30

#### Hydrous Ethanol with Purified Glyceryl Monooleate in Diesel Fuel

Pure glyceryl-1-monooleate was synthesized  
according to the method of Hartman (Chemistry and Industry,  
35 page 711, 1960). The crude product crystallized on stand-  
ing and the crystalline material was verified to be the  
desired product by chromatographic comparison against a

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known standard. There was no contamination with di or triglycerides. 10.0 g of the purified glyceryl-1-monooleate was mixed with 10.0 g hydrous ethanol until a uniform mixture resulted. 80.0 g diesel fuel was then added in portions and mixed thoroughly resulting in a cloudy, semi-stable suspension. 2.7 g of additional purified glyceryl-1-monooleate was added dropwise with mixing until a clear emulsion was achieved with the following final proportions:

<u>Component</u>	<u>Wt. % of Mixture</u>
Glyceryl-1-monooleate	12.4
Hydrous Ethanol	9.7
Diesel	77.9

This emulsion was stable at room temperature but clouded upon chilling for 24 hr. at 1°C. Addition of 0.5 g of glyceryl-1-monooleate rendered the emulsion stable to 0°C but a precipitate formed upon chilling to -13°C for 24 hr. Addition of a further 1.5 g of glyceryl-1-monooleate rendered the emulsion stable even after 24 hr. at -13°C.

Since the glyceryl monooleate is the most expensive component of the hybrid fuel blend, the ability to reduce the quantity needed by nearly two thirds improves the cost-competitiveness of such blends provided that the production cost for purified glyceryl-1-monooleate is not a great deal more than for the industrial grade product, GMOI. Although the direct synthesis route is straightforward, it is likely that the product will cost significantly more. However, preliminary experiments studying the extraction of industrial glyceryl monooleate with methanol suggest that extraction may be an effective alternative and this would not be expected to add appreciably to production costs.

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Example 11Range of Hydrous Ethanol Concentrations with  
Purified Glyceryl Monooleate in Diesel Fuel

5

Portions of hydrous ethanol (190 proof) and pure glyceryl-1-monooleate obtained by direct synthesis were successively added to pure diesel fuel. The added portion of hydrous ethanol would render the mixture cloudy and inhomogeneous but a clear homogeneous emulsion was again achieved when enough glyceryl-1-monooleate was added.

10

Clear emulsions were obtained over the following range of concentrations at 23°C:

15

<u>Component</u>	<u>Wt. % of Mixture</u>
Diesel	57.2 - 95.2
Hydrous Ethanol	1.9 - 27.4
Glyceryl-1-monooleate	2.9 - 15.4

20

The emulsion having the maximum ethanol concentration was stable at room temperature but phase separation occurred upon cooling to 12°C. Upon addition of another 1.7 wt. % of glyceryl-1-monooleate, the emulsion was stable to 0°C.

25

Example 12Hydrous Ethanol with the Ammonium Salt  
of Oleic Acid and purified  
Glyceryl-1-Monooleate in Diesel Fuel

30

Oleic acid was first mixed with hydrous ethanol (190 proof). 28% aqueous ammonium hydroxide was then added and mixed until a clear homogeneous solution was obtained. Diesel fuel was then added in portions and mixed to the following final proportions:

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	<u>Component</u>	<u>Wt. % of Mixture</u>
	Diesel	66.1
	Hydrous Ethanol	17.6
	Oleic Acid	14.7
5	Ammonium Hydroxide	1.6

The resulting emulsion was clear and homogeneous at 23°C.

10 Upon addition of more diesel fuel, phase separation occurred. Glyceryl-1-monooleate obtained by direct synthesis was then added in portions until a clear homogeneous emulsion was obtained with the following final proportions:

15	<u>Component</u>	<u>Wt. % of Mixture</u>
	Diesel	78.7
	Hydrous Ethanol	9.4
	Oleic Acid	7.9
	Ammonium Hydroxide	0.9
20	Glyceryl-1-monooleate	3.1

The emulsion was stable at 23°C. Upon cooling to 12°C, phase separation occurred. Upon addition of 0.5 wt. % glyceryl-1-monooleate, the emulsion was stable to 0°C.

25

#### Emissions Tests

A representative hybrid fuel emulsion, containing 10% wt. hydrous ethanol, has been subjected to emissions tests at the British Columbia Institute of Technology, Vancouver, British Columbia, Canada. For reference purposes, a truck with a newly reconditioned Cummings 6BTA 5.9 L diesel engine was first subjected to emissions tests using pure diesel fuel. A standard pure diesel set of  
35 emission data was then obtained.

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The truck was then fuelled with the hybrid fuel emulsion and run for two days (450 km) before any emissions testing was conducted. No modifications to the truck or engine were made or required. After two days, a set of  
5 emissions data was obtained.

The results of these tests are summarized in the Table below. Emissions data points were selected for comparable RPM's. The data results showed a 65.5% reduction in opacity which correlates with particulate emissions  
10 under the conditions of the test. NOX emissions were also 22% lower. Hydrocarbon emissions were higher for the emulsion but absolute emissions were still very low. Carbon monoxide, carbon dioxide and oxygen levels in the  
15 exhaust were not significantly different between pure diesel and the hybrid fuel.

Reduced opacity and NOX levels were noted for the hybrid fuel throughout the duration of the test runs.

20

DIESEL ENGINE TEST DATA(Vancouver/Wheeler/June 1996)

Test Run	Torque Ft.Lbs. <sup>1</sup>	RPM	Power Hp <sup>1</sup>	Hydrocarbon PPM	Carbon Dioxide %	Carbon Monoxide %	Oxygen %	Opacity %	Nitrogen Oxides PPM
Diesel Control	753	892	81	5.8	8.83	0.01	8.77	10.1	873
Emulsion	534	832	110	7.1	8.47	0.01	9.55	3.48	679
Difference	219	60	-29	-1.3	0.36	0	-0.78	6.62	194
% Difference	29	6.7	-36	-22.4	4.1	0	-8.9	65.5	22.2

<sup>1</sup>Torque should be proportional to Horsepower at constant RPM. The discrepancy needs to be reconciled.

As will be apparent to those skilled in the art in the light of the foregoing disclosure, many alterations and modifications are possible in the practice of this invention without departing from the spirit or scope thereof. Accordingly, the scope of the invention is to be construed in accordance with the substance defined by the following claims.

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## WHAT IS CLAIMED IS:

1. A liquid fuel for use in diesel engines comprising:  
5 (a) about 37 to 96% wt. diesel fuel;  
(b) about 0.1 to about 37% wt. hydrous alcohol;  
and  
(c) an effective amount of a non-ionic surfactant  
used either alone or in combination with one or more fatty  
10 acids and their ammonium salts, the combination of  
ingredients adding up to 100%.
2. A fuel as claimed in claim 1 wherein the hydrous  
alcohol contains about 5% water.  
15
3. A fuel as claimed in claim 1 wherein the hydrous  
alcohol is selected from the group consisting of methanol,  
ethanol, propanol and butanol.
- 20 4. A fuel as claimed in claim 1 wherein the hydrous  
alcohol is hydrous ethanol.
5. A fuel as claimed in claim 4 wherein the hydrous  
alcohol contains about 5% wt. water.  
25
6. A fuel as claimed in claim 1 wherein the non-  
ionic surfactant is selected from the group consisting of  
alkoxyphenol, sorbitan monooleate, oleodiethanolamide and  
glyceryl monooleate.  
30
7. A fuel as claimed in claim 3 wherein the non-  
ionic surfactant is oleodiethanolamide or glyceryl  
monooleate.
- 35 8. A fuel as claimed in claim 4 wherein the non-  
ionic surfactant is glyceryl monooleate.

9. A fuel as claimed in claim 1 wherein the diesel fuel comprises about 37 to 96% wt., the hydrous alcohol is hydrous ethanol and comprises about 2 to about 37% wt., and the non-ionic surfactant is oleodiethanolamide comprising about 27 to 39% wt., the total amount of the components adding up to 100%.

10. A fuel as claimed in claim 1 wherein the diesel fuel comprises about 37 to 96% wt., the hydrous alcohol is hydrous ethanol and comprises about 2 to about 37% wt., and the non-ionic surfactant is glyceryl monooleate comprising about 2 to 39% wt., the total amount of the components adding up to 100%.

11. A fuel as claimed in claim 1 wherein the fatty acid is oleic acid comprising about 9 to 11% wt.

12. A fuel as claimed in claim 9 including about 1% wt. ammonium hydroxide.

13. A fuel as claimed in claim 1 wherein the fatty acid is oleic acid comprising about 13 to 16% wt. and the fuel contains about 1 to 3% wt. ammonium hydroxide.

14. A liquid fuel for use in diesel engines comprising:

- (a) 41 to 59% wt. diesel fuel;
- (b) 2 to about 31% wt. hydrous ethanol; and
- (c) 27 to 39% wt. oleodiethanolamide.

15. A liquid fuel for use in diesel engines comprising:

- (a) 37 to 59% wt. diesel fuel;
- (b) 2 to about 38% wt. hydrous ethanol; and
- (c) 2 to 39% wt. glyceryl monooleate.

16. A method of extending diesel fuel for use in diesel engines which comprises adding to pure diesel fuel between about 0.1% to about 37% wt. hydrous alcohol and an effective amount of a non-ionic surfactant to form a hybrid fuel emulsion which is stable and does not separate into phases at temperatures above -12°C.

17. A method as claimed in claim 16 wherein the hydrous alcohol is hydrous ethanol.

10

18. A method as claimed in claim 16 wherein the non-ionic surfactant is selected from the group consisting of butyl phenoxy  $(CH_2CH_2O)_nH$  wherein n is between about 9 to about 15, sorbitan monooleate, polyoxyalkynol fatty acid ester, oleodiethanolamide, and glyceryl monooleate.

15

19. A method as claimed in claim 18 wherein the hydrous alcohol is hydrous ethanol containing about 5% wt. water.

20

20. A method as claimed in claim 19 including an effective amount of a fatty acid.

21. A method as claimed in claim 20 wherein the fatty acid is oleic acid.

25

22. A method as claimed in claim 20 wherein the fatty acid is in the form of an ammonium salt fatty acid.

23. A method as claimed in claim 22 wherein the fuel includes ammonium hydroxide.

30

24. A method as claimed in claim 23 including glyceryl monooleate.

35

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/CA 98/00562

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C10L1/02 C10L1/18 C10L1/14 C10L1/10

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 451 265 A (SCHWAB) 29 May 1984 cited in the application see the whole document	1-5, 16, 17
A	US 4 083 698 A (WENZEL ET AL.) 11 April 1978 cited in the application see the whole document	1-24
A	EP 0 012 292 A (BAYER AG) 25 June 1980 see claims 1-6	1-24
A	EP 0 012 345 A (BAYER AG) 25 June 1980 cited in the application see the whole document	1-24
A	FR 2 470 153 A (LABOFINA SA) 29 May 1981 see the whole document	1-24
-/-		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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# INTERNATIONAL SEARCH REPORT

International Application No.

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 97 04044 A (EXXON) 6 February 1997 see page 8, line 3; claim 10	1,6-8, 10,15
A	US 4 204 481 A (MALEC) 27 May 1980 see the whole document	1-7,9, 14,16-19

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/CA 98/00562

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4451265	A	29-05-1984	NONE	
US 4083698	A	11-04-1978	US 4002435 A	11-01-1977
EP 12292	A	25-06-1980	DE 2854437 A	26-06-1980
			AT 589 T	15-02-1982
			AU 5392679 A	19-06-1980
			BR 7908184 A	22-07-1980
			CA 1137314 A	14-12-1982
			DD 147683 A	15-04-1981
			JP 55082190 A	20-06-1980
			US 4295859 A	20-10-1981
			ZA 7906800 A	31-12-1980
EP 12345	A	25-06-1980	DE 2854540 A	26-06-1980
			AT 1247 T	15-07-1982
			AU 5392579 A	19-06-1980
			BR 7908185 A	22-07-1980
			CA 1137751 A	21-12-1982
			DD 147854 A	22-04-1981
			JP 55082191 A	20-06-1980
			US 4297107 A	27-10-1981
			ZA 7906799 A	31-12-1980
FR 2470153	A	29-05-1981	LU 81921 A	04-06-1981
			LU 82566 A	20-01-1982
			AT 370764 B	10-05-1983
			AT 552780 A	15-09-1982
			BE 886081 A	07-05-1981
			CH 644889 A	31-08-1984
			DE 3042124 A	11-06-1981
			DK 468980 A	23-05-1981
			GB 2066288 A, B	08-07-1981
			NL 8006041 A	16-06-1981
			PT 72085 B	29-09-1981
			SE 8008173 A	23-05-1981
WO 9704044	A	06-02-1997	AU 6699596 A	18-02-1997
			CA 2182993 A	20-06-1996
			CA 2182995 A	20-06-1996

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Publication No

PCT/CA 98/00562

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9704044	A	CA 2183180 A	20-06-1996
		WO 9618706 A	20-06-1996
		WO 9618707 A	20-06-1996
		WO 9618708 A	20-06-1996
		EP 0743973 A	27-11-1996
		EP 0743974 A	27-11-1996
		EP 0743972 A	27-11-1996
		EP 0839174 A	06-05-1998
		FI 980047 A	13-01-1998
		NO 980143 A	06-03-1998
US 4204481	A	27-05-1980	NONE

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